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(54) Title: TEA PROCESSING WITH ZEOLITES (57) Abstract <p>Tea products, particularly black leaf tea and tea powder, derived from green tea leaf are manufactured by a process involving addition of zeolite, preferably a synthetic sodium or potassium zeolite, for reaction with tea ingredients present or subsequently produced to generate red colour species. The tea products produce beverages having enhanced colour characteristics, in terms of colour properties and speed of colour generation, compared with conventional products. The zeolite treatment can be combined with an acyl-hydrolase, e.g. tannase, treatment.</p>		

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TEA PROCESSING WITH ZEOLITES

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FIELD OF THE INVENTION

10 This invention relates to tea processing and concerns a
method of manufacturing a tea product (particularly black
leaf tea and tea powder) derived from green tea leaf
wherein zeolite is used to generate red colour species.
The invention also concerns tea products and beverages
15 produced from such tea products.

BACKGROUND TO THE INVENTION

20 Processing of green tea leaf to produce a variety of tea
products is well known. In a typical case, freshly
picked green tea leaves are allowed to wither involving
mild drying for up to 24 hours, and the withered leaves
are then cut up in a maceration step in which the leaves
25 are passed through sets of CTC (crush, tear, curl)
rollers that shred the leaves. The shredded leaves are
subjected to a fermentation step for about 2 hours,
during which enzymic oxidation takes place and the leaves
change colour from green to brown as a result of
30 conversion of colourless catechins to coloured
polyphenols including theaflavins (TFs) and thearubigens
(TRs). The product is then dried in a fluidized bed in a
firing stage, resulting in production of black leaf tea
which is sorted and graded. The black leaf tea may then
35 be used in conventional manner, by infusion in water

(usually hot) to produce a red-brown coloured beverage.

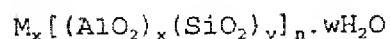
The black leaf tea may alternatively be further processed to produce tea powders with specific desired properties such as solubility in cold water, clarity, colour and taste. A typical use of such powder is as an ingredient in an instant tea powder mix. Alternatively, the tea powder may be used to produce tea based soft drink beverages such as those sold under the Trade Mark LIPTONICE.

As a further possibility, tea powder may be produced from green tea leaf by a slurry fermentation process. Green tea leaf is macerated by passage through sets of CTC rollers and then slurried in water to produce a dilute slurry of macerated tea leaf. The slurry is fermented at a temperature of about 25°C by bubbling air or oxygen through the slurry for a suitable time. The resulting product undergoes a deleafing process in which insoluble material is removed and discarded, leaving a pale coloured solution of tea solids. The solution is concentrated, polished and freeze or spray dried to produce water soluble tea powder.

An important consideration in tea processing is the colour of the ultimate tea or tea-based beverage to be drunk by a consumer, it being desirable for the beverage to be clear and have a bright red-yellow colour so that the beverage looks attractive.

The present inventors have surprisingly discovered that use of zeolites in the manufacture of tea products has a desirable effect on the colour of tea beverages produced therefrom.

Zeolites are a large family of aluminosilicate minerals (both natural and synthetic) having a negatively charged framework structure with cavities housing cations typically of one or more alkali or alkaline earth metals such as sodium, potassium, magnesium, calcium and barium. The general formula of zeolites is:



where:

n = valence of cation or cations M

w = number of water molecules per unit cell

x and y = total number of tetrahedra per cell

It is known to use zeolites, particularly zeolite Y, for decaffeination purposes. See, for example, EP 0013451 (Union Carbide), EP 0042294 (General Foods) and CA 2047500 (Jacobs Suchard).

SU 1342470 (Georgian Institute of Subtropical Industries) describes drying of tea leaves for black tea production in which drying air is first passed through a layer of zeolite before being passed up through a layer of green leaves, with the aim of reducing the humidity of the air to shorten drying times. Subsequent processing is conventional. The zeolite does not contact the leaves, and has no direct involvement in tea processing reactions.

JP 63-24850 (Soft Silica KK) describes use of zeolite, particularly soft porous silicate China clay, in processing of green tea with the aim of removing contaminating ions. Zeolite powder or supernatant liquid obtained by mixing zeolite with water is added to fresh leaf prior to or during the steaming stage of production

of green tea. This results in production of tea with improved aroma, taste and colour. Green tea production does not involve production of the red/brown colours appropriate to black tea products.

5

It is also known from JP 04-330908 (Shinozaki) to incorporate calcined zeolite in filter paper, with the aim of eliminating filter paper odour and dissolved filter paper microparticles. Such zeolite-containing filter paper may be used as material for a tea bag containing black tea.

10

UK patent specification GB 1,382,896 (The Procter & Gamble Company) discloses a method of carbonating aqueous beverages that involves using crystalline aluminosilicates containing gaseous carbon dioxide as a "molecular sieve".

15

However the present invenors are not aware of any prior disclosure of use of zeolites in the manufacture of tea products to generate red colour species.

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25 SUMMARY OF THE INVENTION

In one aspect, the present invention provides a method of manufacturing a tea product derived from green tea leaf, characterised by addition of zeolite to green leaf or green leaf-derived material during tea product manufacture for reaction with tea ingredients present or subsequently produced to generate red colour species.

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Experiments indicate that zeolite can be added at any convenient stage during tea product manufacture, eg

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during processing as outlined above.

For example, zeolite can be added during manufacture of black tea from green leaf. Zeolite is preferably added
5 before or during the fermentation stage, more preferably immediately before the last CTC stage.

In a preferred aspect the invention thus provides a method of manufacturing black tea from green tea leaf,
10 wherein zeolite is added to green leaves prior to or during fermentation.

The resulting black tea is found on infusion to produce a beverage having enhanced colour characteristics compared
15 with a beverage from a similarly produced black tea without zeolite addition. Furthermore, the zeolite treated product develops desirable colour characteristics on infusion more rapidly than would otherwise be the case, even when infused with cold water rather than hot
20 water. The invention can thus provide a fast infusing and/or cold water infusing black leaf tea.

The resulting black tea may optionally be further processed, eg as outlined above, to produce tea powder
25 (hot or cold water soluble) that is also found to have enhanced colour generation properties.

Zeolite can alternatively be added during manufacture of tea powder (hot or cold water soluble) from green leaf.
30 Zeolite is preferably added before or during the slurry fermentation stage.

In another preferred aspect the invention provides a method of manufacturing tea powder from green tea leaf,
35 wherein zeolite is added to green leaves prior to or

6.

during slurry fermentation.

Another approach is to add zeolite during processing of black leaf tea to produce tea powder (hot or cold water soluble), for example as described above.

Zeolite may, as a further possibility, be added during a black and/or green tea extraction process for manufacture of tea powder (hot or cold water soluble). Such processes conventionally involve mixing green and/or black tea leaf with water and subjecting the mixture to a hot water extraction process at a temperature exceeding 50°C with addition of further water. Enzyme treatment with tannase and other enzymes may optionally be carried out prior to extraction. After extraction, the material undergoes deleafing, concentrating, polishing and freeze or spray drying steps, to produce a water soluble tea powder. In this case, zeolite is preferably added prior to the hot water extraction stage.

The invention results in production of tea powder (hot or cold water soluble) that has enhanced colour characteristics on addition of water compared with conventionally produced tea powders. The colour is also found to be acid stable and is not significantly affected at pH of 4 or lower, unlike the colour produced by some conventional tea powders.

The tea powder may be used as an ingredient in an instant tea powder mix or a tea-based soft drink.

Without wishing to be bound by theory, it is thought that zeolites act to promote production of desirable red colour species by their effect in raising pH and causing metal ion exchange.

It is preferred to use synthetic zeolites for reasons of purity and consistency.

5 It is also preferred to use zeolites having a relatively high ratio of aluminium to silicon, and consequently having high metal ion exchange capacity, with the ratio of Si:Al preferably being 2:1 (ie $y = 2x$ in the general formula above) or less, and with the Si:Al ratio more preferably being 1:1 ($x = y$).

10 Preferred zeolites include zeolite A, which has the general formula $M_{12}[(AlO_2)_{12}(SiO_2)_{12}]_n \cdot w H_2O$, ie Si:Al = 1:1. Forms of zeolite A include the sodium form, which has cages or pores with a diameter of 4Å (this is known as
15 zeolite A), and has the formula $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27 H_2O$. Zeolite 4A (with sodium ions) is commercially available under the Trade Names WESSALITH P (from Degussa) and DOUCIL P (from Crosfield).

20 Other forms of zeolite A include:
Zeolite 3A = K form (less voidages, 3Å diameter cages)
Zeolite 5A = Ca form (fewer cages due to divalent cation, 5Å diameter cages).
CG180 (from Crosfield) is a sodium analogue of zeolite
25 3A, having sodium ions in 3Å diameter cages.

It is believed that sodium zeolites can suppress astringency and bitterness in tea based beverages. However those characteristics are perceived by some
30 consumers as being important contributors to the character of tea. It may be desirable to use a potassium zeolite instead, particularly a 3A potassium zeolite, which typically does not have the same suppressing effects. Magnesium and calcium zeolites do
35 not seem to significantly suppress astringency and

bitterness but they tend to generate fewer red colour species colour than that sodium or potassium zeolites. Consequently, a mixture of zeolites may be used to cater to a variety of colour and taste preferences.

5

It is found that addition of even small amounts of zeolite can have a significant effect on the colour of beverages obtained from the tea products, with increasing amounts of zeolite having an increasing effect on colour until a plateau or saturation effect occurs. Zeolite is suitably added at a level as low as about 0.05% zeolite by weight based on initial dry weight of tea leaf. The zeolite can be regarded as a process aid.

10

The tea manufacture methods of the invention are preferably carried out in such a way as to promote generation of theaflavins, as this results in enhanced colour effects. Various techniques for increasing theaflavin levels are known to those skilled in the art. A preferred approach is to use an acyl-hydrolase such as tannase or Teazyme C prior to fermentation to cause degallation and thereby increase theaflavin levels. Further, it is known that different varieties of tea produce varying levels of theaflavins, so high theaflavin-producing tea varieties can be used to advantage.

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The present invention can thus enable production of tea products, particularly black leaf tea and tea powders (hot and cold water soluble), that produce beverages (including tea based soft drinks) that have enhanced colour characteristics as compared with conventionally produced products. The invention can also promote production of cold water soluble colour species, leading to the possibility of fast infusing and/or cold infusing

tea products.

5 The invention also includes within its scope tea products and beverages, particularly black leaf tea, tea powders, instant tea powder mixes and tea-based soft drinks, produced by a method of the invention, including beverages having a (final) pH of 4 or lower. Tea based beverages, particularly ready to drink tea products, preferably have a pH between 3 and 4 to maximise taste and colour stability.

10 In another aspect the invention covers use of zeolite to produce red colour species in tea products and tea beverages.

15 The invention will now be further described, by way of illustration, in the following Examples and with reference to the accompanying drawings, in which:

20 Figure 1 is a flow chart illustrating a slurry fermentation process for manufacture of tea powder from green leaf;

25 Figure 2 is a flow chart illustrating a process for manufacture of black leaf tea from green leaf;

Figures 3a and 3b are graphs of absorbance (445nm) versus time (seconds); and

30 Figure 4 is a flow chart illustrating an extraction process for manufacture of tea powder from black or green leaf.

EXAMPLE 1

Black Tea Powder Produced by Slurry Fermentation

5 Referring to Figure 1, a conventional slurry fermentation process for production of tea powder from green leaf comprises cutting, slurry fermentation, deleafing, concentration, polishing and freeze or spray drying steps. In accordance with the invention, in this example
10 zeolite is added prior to the slurry fermentation step. Tannase is preferably also added prior the slurry fermentation step, before zeolite addition.

Experiments were carried out using green leaf from Kenyan
15 tea clones. All two leaves and a bud were picked and used fresh (ie no withering, freezing etc). The fresh leaf was plucked and then passed through a CTC (cut, tear, curl) machine to produce dhool (macerated, unfermented green leaf) which was then used for the
20 following experiments.

In a control experiment 40.7 ml of distilled/deionised water was placed into a 250ml shake flask. To this 11.9g of dhool was added (making a 5% solution dry basis).
25 This solution was placed on a shake flask and aerated and mixed at 25°C at 200 rpm for 75 minutes. The solution was then deleafed by passing it through a 180 µm sieve.

The deleafed liquor was placed for 30 minutes at 4°C then
30 centrifuged (de-creamed) at 12,000 g at 4°C for 25 minutes.

The above experiment was then repeated, with conditions identical to the control except that 0.5g of zeolite 4A
35 (WESSALITH P) was added to the water in the shake flask.

This is approximately equivalent to 1g of zeolite to 5g of black tea leaf. Thus zeolite was present during fermentation. All zeolite was removed during the de-creaming phase.

5

The % cold soluble tea solids (%CSS) was measured on the de-creamed liquor. The HunterLab UltraScan XE was used to measure colour using the CIE Lab scale (2° observer, illuminant C & 1 cm pathlength). Colour is measured and represented by three colour dimensions, L, a and b. L represents paleness/darkness, with L = 0 being black and L = 100 being white or colourless. a represents redness/greeness, with high positive values of a being red and high negative values of a being green. b represents blueness/yellowness, with high positive values of b being yellow and high negative values of b being blue.

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The L*a*b values for the de-creamed solution were taken and this solution was diluted using pH 3.7 citrate/phosphate buffer to obtain colour measurements at various concentrations and hence determine the L*a*b values at 0.32% CSS (drink strength).

25

Results and Observations

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During fermentation the slurries containing zeolite went a deep mahogany red instead of green/brown. Dilution of zeolite-treated slurries with buffer during colour measurement caused the solution to flock and some of the precipitate (and colour) to fall out. The following colour measurements were obtained.

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All at 0.32% CSS	L	a	b
Control	91.7	4.8	73.5
Zeolite addition	70.0	24.0	92.5

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A second series of similar experiments was carried out adding zeolite 4A (WESSALITH P) (0.3g zeolite/0.32g powder) to slurry fermented powders (control and tannase treated) (tannase addition was 0.0064% of weight of tea solids). This is approximately equivalent to 1g zeolite to 3.5 of black leaf tea. Dramatic changes in colour were observed.

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	L	a	b
Control	85	2	83
Control + Tannase	79	15	104
Control + Zeolite	60	28	80
Control + T + Z	50	48	74
Control + T + Z (pH 3.7)	61	35	83

The colour is somewhat unstable and some colour irreversibility is observed in the pH 3.7 citrate/phosphate buffer used. Subsequent experiments have shown that the precipitation and colour loss is less evident when using either acetic acid or a citric/citrate buffer.

EXAMPLE 2

Black Leaf Tea Produced from Green Leaf

Referring to Figure 2, a conventional process for manufacture of black tea from green leaf comprises 4 cutting (CTC) stages, fermentation, firing and grading steps. In accordance with the invention, in this example zeolite is added prior to the fermentation step, immediately before the final CTC stage. Tannase is preferably added during cutting, before zeolite addition.

Experiments were carried out using withered green leaf from Kenyan and Sri Lankan tea clones. Processing steps were as follows:

- 5 1. The leaf was comminuted by three successive CTC treatments.
- 10 2. The resulting dhool was spread onto a stainless steel tray and sprayed with an aqueous tannase solution. After each coverage the dhool was mixed by hand and the process repeated until all the enzyme had been applied. 10ml of distilled water containing 2000U of tannase was applied for each 300g of dhool. The treated dhool was then transferred into a polythene bag and the air
15 expelled to form a limited oxygen environment. The bag was sealed and dhool left to incubate for 30 minutes at room temperature (18°C).
- 20 3. The dhool was spread onto a stainless steel tray and 6 grams of powdered zeolite 4A (WESSALITH P) mixed by hand until a homogenous blend was obtained. This is approximately equivalent to 1g of zeolite to 16g of black leaf tea.
- 25 4. The treated dhool was then passed through the CTC process a final time. This CTC pass has three possible effects:
 - 30 i) To further comminute the leaf such that the leaf size range becomes compressed around the median value. This will result in a tighter distribution of leaf particle size sieving and also help to negate experimental errors arising during infusion due to differing leaf surface areas.

ii) To disrupt any leaf aggregates formed after the addition of water during the tannase treatment. This will result in a more efficient fermentation.

5 iii) To absorb the solid zeolite into the leaf tissue. The CTC mechanism compresses the comminuted leaf like a sponge, resulting in the zeolite powder being drawn into the leaf structure as the leaf fragment expands when leaving the CTC rollers. If zeolite is added and this
10 final CTC stage omitted, the infused product is extremely hazy due to solid, unbound, zeolite being released into the liquor from the leaf surface.

5. The treated dhool was then transferred into
15 perforated stainless steel trays for fermentation in an environmental cabinet. The dhool was loosened to allow good aeration and incubated for 180 minutes at 95% relative humidity (RH).

20 6. The fermented dhool was fired for 6 minutes at 125°C followed by 8 minutes at 80°C in a fluid bed drier. The temperatures refer to an inlet air temperature and do not necessarily reflect the temperature of the dhool during each stage of firing.

25 7. The fired leaf was graded to between 1.13mm and 0.355mm by sieving. This was to ensure that abnormal leaf sizes such as dust and/or aggregates did not affect infusion by varying the surface area.
30

Summary of Experimental Manufacturing Processes

Control Samples : Steps: 1, 4, 5, 6, 7

Tannase Treated Samples : Steps: 1, 2, 4, 5, 6, 7

5 Zeolite Treated Samples : Steps: 1, 3, 4, 5, 6, 7

Tannase and Zeolite Treated Samples : Steps: 1, 2, 3, 4,
5, 6, 7

Infusion Methodology

10

All experimental results refer to the colour and properties of a cold infused liquor. The water temperature was approximately 18°C. The infusions were prepared by using the following method:

15

i 2.27g of leaf tea was heat sealed into a nylon bag of tetrahedral form having sides of about 60mm.

20

ii The bag was placed into a beaker containing 200ml of distilled water and infused for 5 minutes in a quasi-static state. The infusion method was the a model of a consumer system, and consisted of the infusion being stirred 5 times immediately after adding the bag. At the end of the 5 minute period the infusion was stirred 5
25 more times and the bag squeezed to expel residual liquor. The spent bag was then discarded.

30

iii The resulting liquor was then analysed colorimetrically via transmittance on a Minolta Chroma Meter and haze readings were recorded using a DrLange instrument. The soluble solids were determined using the oven method and recorded as a percentage value.

Experimental results

5 The following results (recorded in duplicate) were
obtained. All treatments and measurements were carried
out at the same time on the same leaf batch allowing good
comparative data to be obtained.

5

Sample	L-value	a-value	b-value	Haze	% Solids
Kenyan Control	91.53	-3.42	44.64	9.1	0.1612
	90.93	-3.41	46.18	10.0	0.1672
Kenyan & Tannase	87.65	-2.24	74.08	10.9	0.2083
	86.88	-1.66	76.15	11.6	0.2174
Kenyan & Zeolite	79.52	8.34	50.39	NR	0.1618
	79.24	2.96	50.28	NR	0.1609
Kenyan & Tannase & Zeolite	49.75	45.96	73.35	NR	0.2373
	47.62	48.87	75.53	NR	0.2615
Sri Lankan Control	92.12	-4.21	35.90	11.5	0.1595
	92.22	-4.33	36.30	15.1	0.1603
Sri Lankan & Tannase	89.80	-5.06	56.60	15.3	0.2153
	89.75	-5.03	56.46	16.7	0.2127
Sri Lankan & Zeolite	82.55	3.51	34.80	NR	0.1603
	83.81	2.96	33.55	NR	0.1546
Sri Lankan & Tannase & Zeolite	65.05	27.61	61.86	NR	0.2315
	67.65	25.77	60.30	NR	0.2219

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NB: Haze analysis results were not recorded as the colour intensity of the sample gave greatly elevated readings.

The results demonstrate the following trends:

- 5 a) The zeolite treatment appears to have minimal or no effect on the levels of tea solids in the infusion, or on the b-value during colour measurement. The major effects are to decrease the L-value and increase the a-value, resulting in a darker, redder, infusion.
- 10 b) Combining tannase and zeolite treatment results in an enormous increase in the colour of the infused liquor. It can be inferred that the improvements in the b-value is tannase derived, while the improvements in the L-value and the a-value are zeolite derived. This would explain why the combined effects of tannase and zeolite appears
- 15 to have a greater effect than if each were used individually. An interesting point is the apparent increase in the percentage solids when both tannase and zeolite are used compared to simply adding tannase. As zeolite alone does not increase the solids level, it
- 20 would be expected that this value would be equivalent to that seen for the tannase treatment, and therefore the reason for this increase remains unresolved.
- 25 c) As a final point, the behaviour of the two tea types, ie Sri Lankan and Kenyan, after addition of tannase and/or zeolite follows the same trends. The absolute differences in the values obtained demonstrates the different composition and properties of the leaf types and not differential effects of the treatments
- 30 used.

Overall, the results indicate the treatment of dhool with zeolite before fermentation leads to a considerable increase in colour species generation, and results in a

35 final infusion product which is darker and redder than an

untreated control. The colour increase is greater than that seen after tannase treatment of the dhool at the same stage of the manufacture process, but unlike tannase no increase in tea solids is detectable in the infusion product.

The effects of zeolite and tannase are synergistic, with the colour of the infusion product being greater than the additive effects of tannase and zeolite when added individually. This would indicate that the oxidative mechanism of the zeolite reaction is either able to use "substrates" generated by the esterase activity of tannase to produce a more highly coloured species and/or is able to facilitate the generation of an excess of the same colour species as released by the tannase digest.

The experimental results to date indicate that the tannase and zeolite treatments can be ranked by the degree of colour generation in an infused product as follows:

Control < Tannase < < Zeolite < < < Tannase +
Zeolite

EXAMPLE 3**Fast Infusing Leaf Tea**

5 Black tea was manufactured as described in Example 2.
Control black tea preparation required steps 1, 4, 5 and
6. Zeolite treatment required steps 1, 3, 4, 5 and 6.
In addition both samples were graded between 0.500mm and
0.250mm by sieving. Teabags were made with inner
10 dimensions of 54mm x 64mm (equivalent to a UK teabag)
using JR. Crompton 482901 heatseal paper (this being a
good quality teabag paper). The bags were filled with
3.125g (+/-0.001g) of each of the tea samples. The
resulting teabags were infused in 250cm³ freshly boiled
15 deionised water. The teabags were subjected to two
methods of infusion: (i) dynamic infusion [continual
agitation simulating that of a consumer dunking]; and
(ii) static infusion [the bag held vertically in the
liquor simulating a pot brew].

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The resulting liquor (unmilked) was pumped to a
spectrophotometer and absorbance variation with time
measured. The wavelength used (445nm) correlates well to
UK consumer acceptance and with solids eluted. Results
25 are shown graphically in Figure 3a (dynamic infusion) and
Figure 3b (static infusion), with some values being set
out below.

30

	Dynamic		Static	
	Abs. at 30s	Abs. at 60s	Abs. at 60s	Abs. at 120s
Control		2.3834		0.3619
Zeolite Treated	2.3454		0.3702	

The infusion curves of Figure 3 demonstrate the reduction in brew time that can be achieved by using zeolite treated tea. In a dynamic (mug brew) situation zeolite treated tea produces an infusion equivalent to a 60 second control brew in 31 seconds (ie. just over half the time). In a static (pot brew) situation, a brew equivalent to 120 seconds in terms of optical density is achieved in 50% of the time (ie. 60 seconds).

EXAMPLE 4**Cold Infusing Leaf Tea**

5 Further experiments, generally similar to those described
in Example 2, were carried out to produce cold infusing
black leaf tea from green leaf, using different zeolites
at different levels. The zeolites used were zeolite 4A
(WESSALITH P and DOUCIL P) and zeolite P (CG 180 from
10 Crosfield).

Manufacture

Frozen withered Kenyan leaf stored at -80°C, is CTC
15 treated twice to comminute the leaf. 200g of the
resulting dhool (equivalent to 63g of black tea) is
spread evenly on a stainless steel tray to give a bed
thickness of approximately 0.5cm, and sprayed with 10.0ml
of distilled water containing 100U of Kikkumen of tannase
20 (equivalently to 2.0mg). The dhool is mixed by hand
after the first 5.0ml has been applied. The treated
dhool is sealed in a plastic bag and the excess air
expelled to produce a reduced oxygen environment, before
incubation at 20°C for 30 minutes. After incubation the
25 dhool is transferred to a stainless steel tray and spread
out as before 4.0ml of distilled water containing 0.5g of
zeolite in suspension is sprayed onto the dhool, again
with mixing, before a final CTC pass which serves to
further comminute the leaf, further distribute the
30 zeolite, and cause the zeolite to be absorbed into the
leaf structure. This is approximately equivalent to 1g
of zeolite to 125g of black leaf tea.

The tannase and zeolite treated leaf is then fermented
35 for 150 minutes at 18°C with 95% relative humidity to

allow the oxidative reactions to take place. The fermented dhool is then fired in a fluid bed dryer using hot air at 125°C for 6 minutes followed by 80°C for 8 minutes to produce the final tea product.

5

Infusion (Loose Leaf)

2.27g of the tea product is weighed into a conical flask. 200ml of cold water (17°C-20°C; tap or distilled) is poured onto the leaf, and the infusion stirred for 5 minutes at approximately 150rpm. The resultant liquor is filtered through a Whatman 540 filter paper to remove the spend leaf, which is squeezed to extract residual liquor before discarding. The liquor volume is restored to 200ml before colour evaluation using Minolta transmittance.

10
15

Typical Infusion Results

20

Effect of Zeolite Type

With distilled water:

25

Sample	L-value	a-Value	b-Value	Haze	%Solids	pH
Kenyan Control	91.25	-2.77	48.82	5.0	0.184	5.40
Tannase (100U) Treated Kenyan	88.83	-2.40	67.36	7.3	0.217	5.03
Kenyan - 100U Tannase & 0.5g CGI80	83.75	4.88	71.34	9.5	0.224	5.27
Kenyan - 100U Tannase & 0.5g Wessalith-P	88.70	-0.47	62.63	4.1	0.192	5.23
Kenyan - 100U Tannase & 0.5g Doucil-P	83.68	3.62	74.11	12.0	0.231	5.20

30

35

25

With tap water:

Sample	L-value	a-Value	b-Value	Haze	†Solids	pH
Kenyan Control	89.91	1.13	28.17	4.4	0.182	6.90
Tannase (100U) Treated Kenyan	85.40	2.28	41.58	2.6	0.196	6.73
Kenyan - 100U Tannase & 0.5g CG180	82.13	8.47	47.77	3.2	0.225	6.71
Kenyan - 100U Tannase & 0.5g Wessalith-P	83.95	6.78	45.00	2.9	0.217	6.67
Kenyan - 100U Tannase & 0.5g Doucil-P	83.07	6.90	45.87	3.2	0.213	6.69

Effect of Amount of Zeolite (WESSALITH-P)

Experiments were carried out using the same, lower (0.05g) and higher (1.0g) levels of zeolite. The lower and higher levels of zeolite are approximately equivalent to 1g of zeolite to 1250g and 63g of black leaf tea, respectively.

26

With distilled water:

Sample	L-value	a-Value	b-Value	Haze	%Solids	pH
Kenyan Control	89.75	-2.78	55.09	10.3	0.226	4.96
Tannase (100U) Treated Kenyan	87.46	-1.02	73.66	12.0	0.270	4.42
Kenyan 100U Tannase & 0.05g Wessalith-P	84.42	2.05	81.96	14.0	0.280	4.51
Kenyan - 100U Tannase & 0.1g Wessalith-P	84.18	2.13	81.91	18.0	0.281	4.54
Kenyan - 100U Tannase & 0.5g Wessalith-P	82.26	7.20	79.25	11.3	0.263	4.82
Kenyan - 100U Tannase & 1.0g Wessalith-P	74.85	19.37	72.03	13.2	0.262	5.11

20

With tap water:

Sample	L-value	a-Value	b-Value	Haze	%Solids	pH
Kenyan Control	90.34	1.18	29.96	6.4	0.198	6.78
Tannase (100U) Treated Kenyan	83.34	7.01	56.16	6.8	0.269	6.48
Kenyan - 100U Tannase & 0.05g Wessalith-P	81.38	10.46	58.84	4.7	0.264	6.44
Kenyan - 100U Tannase & 0.1g Wessalith-P	78.84	13.81	62.78	7.0	0.286	6.40
Kenyan - 100U Tannase 0.5g Wessalith-P	76.54	18.82	54.56	5.3	0.266	6.43
Kenyan - 100U Tannase & 1.0g Wessalith-P	79.04	15.11	46.58	3.9	0.250	6.58

40

EXAMPLE 5Conversion of Black Leaf Tea to Powder

5 Sri Lankan black leaf tea was produced as described in Example 2, and the leaf was then converted to black tea powder. This involved extracting the leaf with water at a water:leaf ratio of 15:1, at a temperature of 80°C for
10 2 minutes. Spent leaf and fines were filtered off but not centrifuged. Liquor was freeze dried under standard conditions to produce black tea powder.

15 Milked liquor was prepared from the powder by addition of boiling demineralised water and whitener (in the form of a commercially available non-dairy creamer known as DP355 from DMV) in the following proportions: 0.4% tea powder and 2.5% whitener in 100 ml of water (further details are given below).

20 Colour was measured using a 2mm pathlength as described below.

Milked Tea Liquors - Measurement of Appearance

25 This method measures colour by reflectance. Tea samples containing milk/whitener are translucent, rather than opaque, so extra care must be exercised in both measuring and interpreting results. The equipment geometry, colour
30 scale, cell path length, observer angle illuminant and colour indices should be appropriate for the investigation or product application. Changes in powder concentration are known to affect the light
35 absorbing/scattering of the liquors in a non-linear way. This method was devised to give reproducible results and

the measurements are made at 20°C not at hot make-up or warm drinking temperature where colour changes are rapid during cooling. Measurement of L, a, b, K/S, opacity, dominant wavelength or excitation purity will not
5 represent the true visual appearance of consumer made samples but will provide good quality comparative data. The use of milk (whole or semi-skimmed) is not recommended, due to batch to batch variation in the protein content and fat cell size distribution, which
10 will have a considerable effect on the results.

Colour Measurement: Standard Method - HunterLab
Ultrascan

15 1. For powder tea, make up a 1.0% dispersion/solution. Dissolve 2.5g in 50ml of boiling deionised water and cool rapidly. Make up to 250ml, with deionised water, in a volumetric flask. From this 1% stock solution make up 100ml of each of the following concentrations: 0.1, 0.2,
20 0.3, 0.4, 0.5, 0.6%. Add 2.5gm whitener DP355 to each 100ml of tea solution. Alternatively add 10ml of 25% whitener DP355 premade hot and cooled. N.B. results from different whitener methods are not comparable.

25 2. For whiteners, make up a 25% dispersion/solution. Dissolve 15 gm in 60ml hot water and cool rapidly. Make up 500ml of 0.4% tea solution using a standard tea powder as described above e.g. Ceytea 140X. To 100ml aliquots of the tea solution add whitener solution to give each of
30 the following concentrations 1.5% (6ml), 2.0% (8ml), 2.5% (10ml), 3.0% (12ml), 3.5% (14ml). Mix thoroughly. For full fat milk powders of high fat whiteners (>40% fat) add half this amount of whitener dispersion (or use manufacturers recommended level). Alternatively weigh
35 out the correct weight of dry whitener to achieve the

desired concentrations, add tea powder (0.4g), mix and add 30ml hot deionised water and cool rapidly. Make up to 100ml in a volumetric flask. N.B. results from different make up methods are not comparable.

5

3. Measure after 1 hour rest at 20°C.

10

4. Set Hunterlab Ultrascan to measure with reflectance, specular include (RSIN), D65 illuminant, 10°C observer angle and opacity procedure.

5. Calibrate/standardize sensor.

15

6. Pour sample into 2mm path length cells with black and white backgrounds to within 2mm of top. Place at reflectance port and take readings. Repeat measurements to give 3 replicates. This data is used for the calculation of all values.

20

7. Whilst the data once collected may be manipulated and presented in many different ways, there are some conventions which should normally be observed, e.g. L, a, b data should normally only be presented as a 3D plot and K/S value at the dominant wavelength.

25

Appearance details of the milked liquors are set out in the following table.

30

Sample	Milk Liquor Colour			Comments
	L	a	b	
Control	63.3	13.7	34.0	hue angle: 68.1° chroma: 36.7 Yellow and bright with reasonable colour intensity
Zeolite	56.1	10.6	23.3	hue angle: 65.5° chroma: 25.6 Very dark and dull. Much less yellow than control
Tannase	66.8	12.1	34.6	hue angle: 70.7° chroma: 36.7 Vibrant yellow. Very intense colour
Zeolite + Tannase	53.6	11.7	20.4	hue angle: 60.2° chroma: 23.5 Reddest. "Muddy" and dull with pinkish hue

5

EXAMPLE 6

Cold Water Soluble Powder from Extraction of Black Leaf Tea

5

Referring to Figure 4, a conventional extraction process for manufacturing tea powder from green and/or black leaf comprises mixing, extraction through to drying, 10 deleafing, concentrating, polishing and freeze/spray drying steps. Conventional enzyme treatment, eg with carbohydrases and/or tannase, may be carried out prior to extraction. In accordance with the invention, zeolite is added, preferably prior to extraction, after 15 conventional enzyme treatment. An alternative approach would be to use zeolite treated green tea as an ingredient in this process.

A blend of 50:50 Sri Lankan High:Low Grown BMF (Broken 20 Mixed Fannings) was used. Two extraction systems were investigated, one with and the other without, enzymes. The enzyme system and levels used were:
Viscozyme (Ex Novo) at 0.5%
Celluclast 1.5L (Ex Novo) at 0.25% and
25 Tannase (ex Kikkoman) 50,000Tau/g at 0.0064% (as % of leaf wt).

Viscozyme is a multienzyme complex containing a wide range of carbohydrases and is produced from a selected 30 strain of the *Aspergillus* group. Celluclast is a liquid cellulase preparation made by submerged fermentation of a selected strain of fungus *Trichoderma reesei*.

The process was based on a total water:leaf ratio of 35 13.5:1 and consisted of two stages:

- (i) Incubation stage at 45°C for 40 minutes, at a water to leaf ratio of 6:1
- (ii) Extraction stage at 80°C for 45 minutes, with the water to leaf ratio increased to 13.5:1.

5

At this point the final extract is deleafed, cooled and held overnight at +4°C, prior to polishing at 15°C, 10,000 RPM for 20 minutes.

- 10 Zeolite 4A (WESSALITH P) additions were investigated at each of the above stages at one or two different levels, ie 1g of zeolite to 14.3g of BMF and 1g of zeolite to 7.15g of BMF.

- 15 Zeolite additions to the deleafed extracts at the same two levels, with and without further heating to 80°C, were also investigated.

- 20 The resultant polished extracts from the trials were freeze dried at 25°C over 2 days.

Colour assessment was carried out on the reconstituted freeze dried tea powders dissolved in 0.02M citrate buffer at 0.32% (w/v) solids concentration, pH 3.7.

- 25 Measurements were made using a Minolta CT-310 instrument using illuminant C, a 2° observer, a 1cm pathlength transmission cell, and the results based on CIE 1976 L*a*b colour space.

- 30 The results are shown in the table below.

Sample/Description	Dissolved Powder Colour			Z:BMF
	L	a	b	
5 1. Control enzyme-based extraction process.	90.45	-3.02	45.04	-
2. Enzyme treatment in presence of zeolite.	75.10	+6.34	58.04	1:14.3
10 3. Zeolite addition to extraction mix post enzyme treatment.	79.35	+4.27	48.45	1:14.3
15 4. Zeolite addition to extract from enzyme-based process.	89.16	-1.98	46.80	1:7.15
5. Zeolite addition to extract plus further heating.	80.09	+2.53	46.91	1:14.3
20 6. Control conventional hot water extraction process.	90.84	-3.28	43.77	-
7. Conventional extraction in presence of zeolite.	73.52	+9.14	54.68	1:14.3
25 8. Zeolite addition to hot extract from standard process.	84.73	+0.10	55.07	1:7.15

EXAMPLE 7

Part 1 - Combining a tannase and potassium zeolite treatment

5

Materials

- Tannase : 50KU/g; Kikkoman, Japan
- TeazymeC : Multifunctional enzyme. Approximate activities :
- 10 Pectin Esterase (800U/ml)
- Polygalacturonase (200U/g)
- Transeliminase (unknown)
- Tannase like (120U/ml)
- Zeolite : Potassium Zeolite (K'zeolite); Crosfields.
- 15 Tea Leaf : Frozen withered leaf; Mabroukie, Kenya.

Withered leaf was comminuted to form dhool by two successive CTC treatments, before spreading the onto a stainless steel tray and spraying with tannase (20 ml

20 aqueous solution containing 100 U of tannase/200 g of dhool). The material was mixed thoroughly by hand and CTC treated to ensure homogenous mixing of the tannase, before fermenting for 75 minutes at 22°C and 95% relative humidity in an environmental cabinet. The leaf was CTC

25 treated after 35 min of fermentation to further mix the dhool and to improve aeration. The dhool was then spread onto a stainless steel and sprayed with an aqueous suspension of zeolite (0.5 g in 20 ml water/200 g of dhool), with mixing by hand to ensure an even coverage.

30 The mixture was CTC treated a final time to mix and incorporate the zeolite before fermenting for 120min at 22°C and 95% relative humidity. The dhool was then fired and the black tea graded to give a leaf size between 0.355 and 1.18 mm before infusion.

35

Infusion

2.27 g of leaf was weighed into a 250 ml conical flask.
200 ml of cold deionised water was added and the
5 suspension stirred for 5 minutes. The spent leaf was
removed by filtration and the liquor made up to 200 ml
with cold tap water in a volumetric flask. Liquor colour
parameters (L a, b, and haze) were measured using the
HunterLab, together with the pH and the % soluble solids.

10

Part 2 - Combining teazyme C and potassium zeolite treatment

5 The leaf manufacture was identical to Part 1 except that the tannase was replaced with a 20 ml aqueous solution containing 0.1 ml teazyme C/200 g of dhool. Liquor preparation and analysis were identical.

Results after cold deionised water infusion

10

Sample Treatment	L-value	a-value	b-value	Haze	pH	% solids
Control	88.51	-0.63	66.13	11.53	5.35	0.23
Tannase & K ⁺ zeolite	78.80	13.92	81.54	28.53	5.49	0.25
15 TeazymeC & K ⁺ zeolite	82.66	8.73	70.02	17.57	5.38	0.24

20 Both systems result in a considerable improvement in cold water infusion performance in the black tea product.

CLAIMS

1. A method of manufacturing a tea product derived from
5 green tea leaf, characterised by addition of zeolite to
green leaf or green leaf-derived material during tea
product manufacture for reaction with tea ingredients
present or subsequently produced to generate red colour
species.
- 10 2. A method of manufacturing black tea from green tea
leaf, wherein zeolite is added to green leaves prior to
or during fermentation.
- 15 3. A method according to claim 2, wherein the black tea
is processed to produce tea powder.
4. A method of manufacturing tea powder from green tea
20 leaf, characterised by addition of zeolite to green
leaves during tea product manufacture for reaction with
tea ingredients present or subsequently produced to
generate red colour species, said zeolite being added
prior to or during slurry fermentation.
- 25 5. A method of manufacturing tea powder from black leaf
tea, characterised by addition of zeolite to green leaf
or green leaf-derived material during tea product
manufacture for reaction with tea ingredients present or
subsequently produced to generate red colour species,
30 said zeolite being added during processing.
6. A method of manufacturing tea powder from black
and/or green tea by an extraction process, characterised
by addition of zeolite to green leaf or green leaf-
35 derived material during tea product manufacture for

reaction with tea ingredients present or subsequently produced to generate red colour species, said zeolite being added during processing.

5 7. A method of enhancing the colour of a sold extracted tea product derived from green tea leaf, characterised by addition of zeolite to green leaf or green leaf-derived material during tea product manufacture for reaction with tea ingredients present or subsequently produced to
10 generate red colour species.

8. A method according to any preceding claim, wherein the zeolite is a synthetic zeolite.

15 9. A method according to any preceding claim, wherein the zeolite has a ratio of Si:Al of 2:1 or less, preferably 1:1.

20 10. A method according to any preceding claim, wherein the zeolite is a sodium, potassium, calcium or magnesium zeolite, or mixtures thereof.

25 11. A method according to any preceding claim, wherein the zeolite is a 4A sodium zeolite or a 3A potassium zeolite.

30 12. A method according to any preceding claim, wherein zeolite is added at a level of at least 0.05% by weight based on initial dry weight of tea leaf.

13. A method according to any preceding claim, wherein an acyl-hydrolase is added to increase the rate at which red colour species are liberated from the tea.

35 14. A method according to claim 13, wherein the acyl-

hydrolase is selected from tannase and Teazyme C.

15. A tea product produced by the method of any one of the preceding claims.

5

16. A tea-based beverage produced from a tea product in accordance with claim 15.

10

17. A beverage according to claim 16, having a pH of 4 or lower.

18. Use of zeolite to produce red colour species in tea products and tea beverages.

15

19. Use of an acyl-hydrolase in combination with zeolite to increase the rate at which red colour species are liberated from black tea in cold water.

Fig.1.

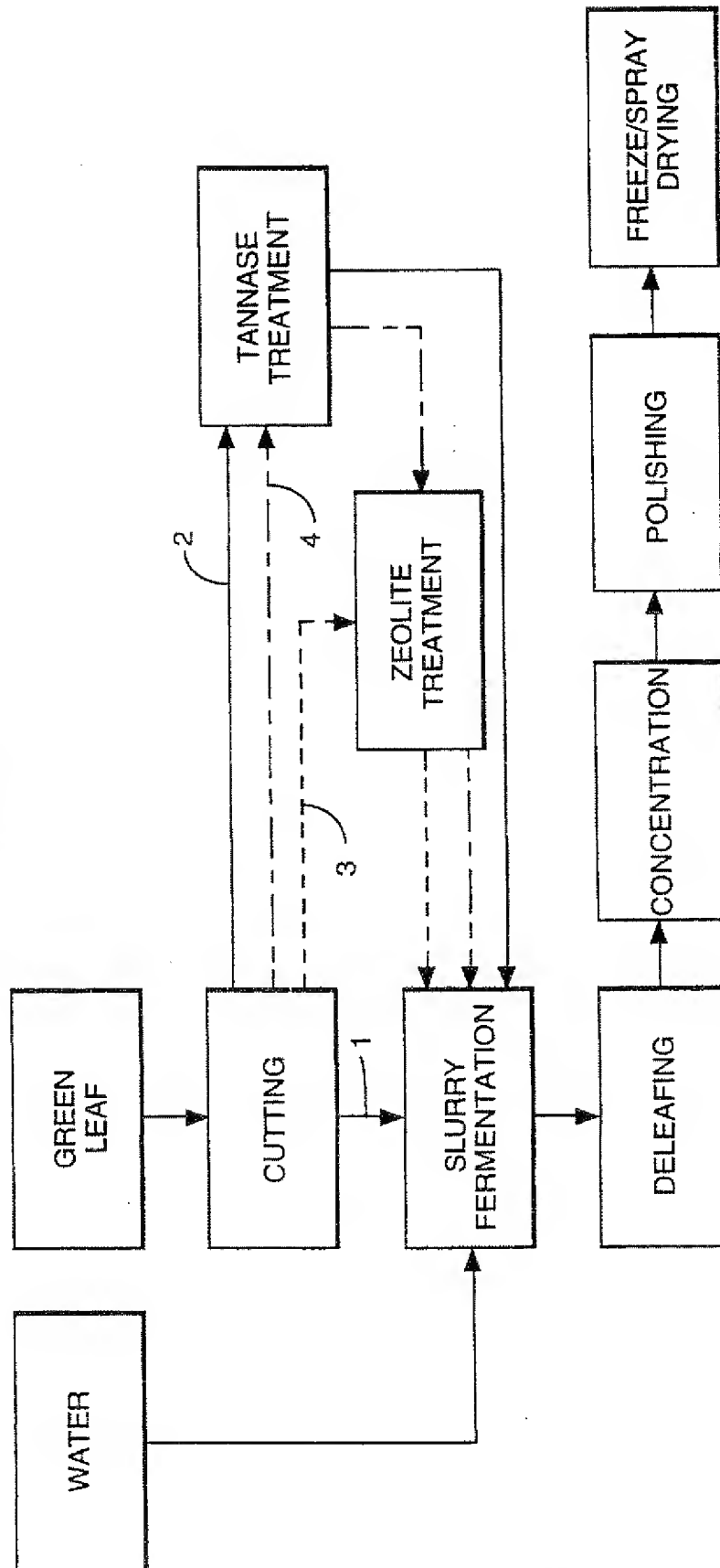


Fig.2.

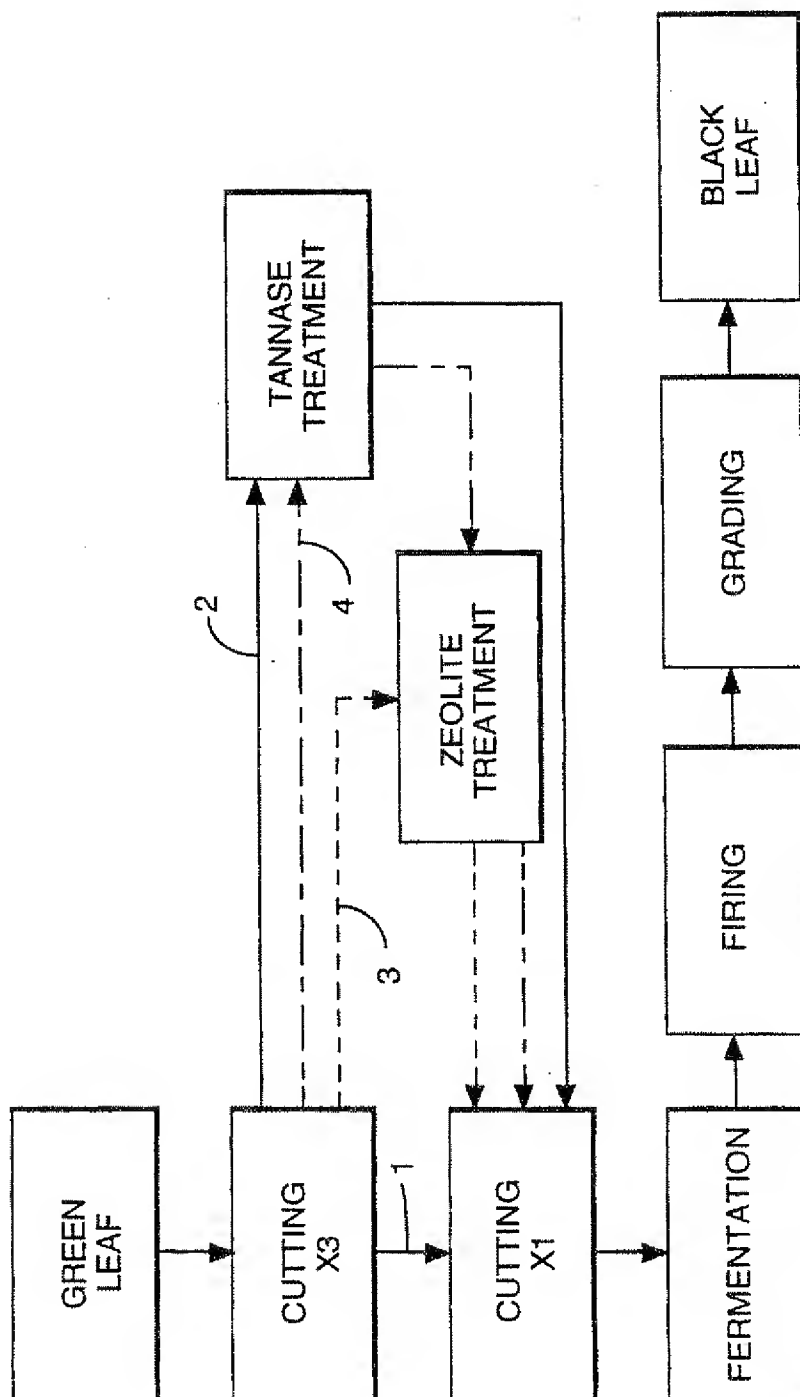


Fig.3A.

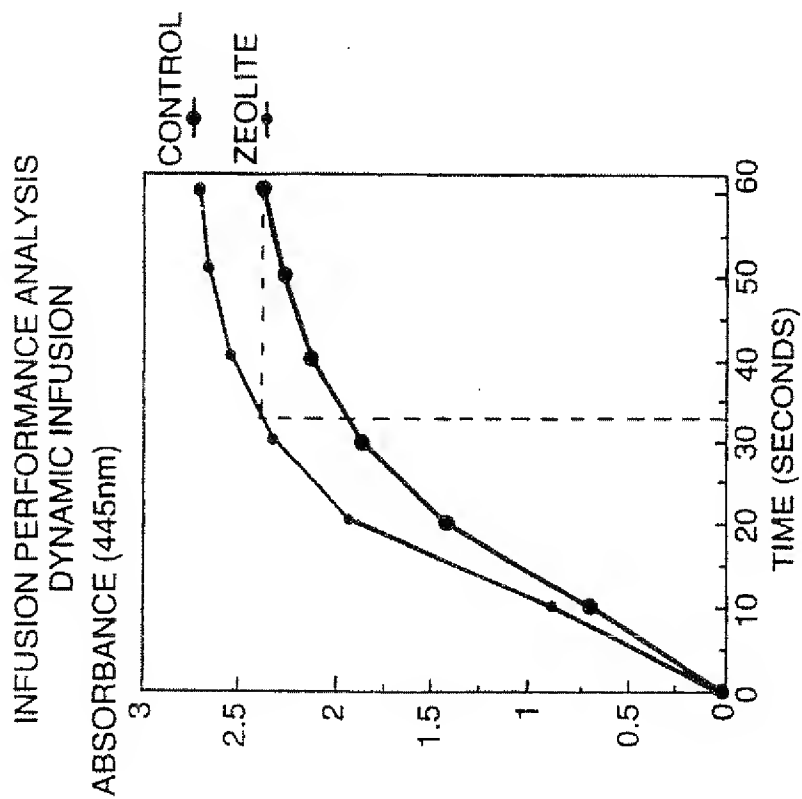
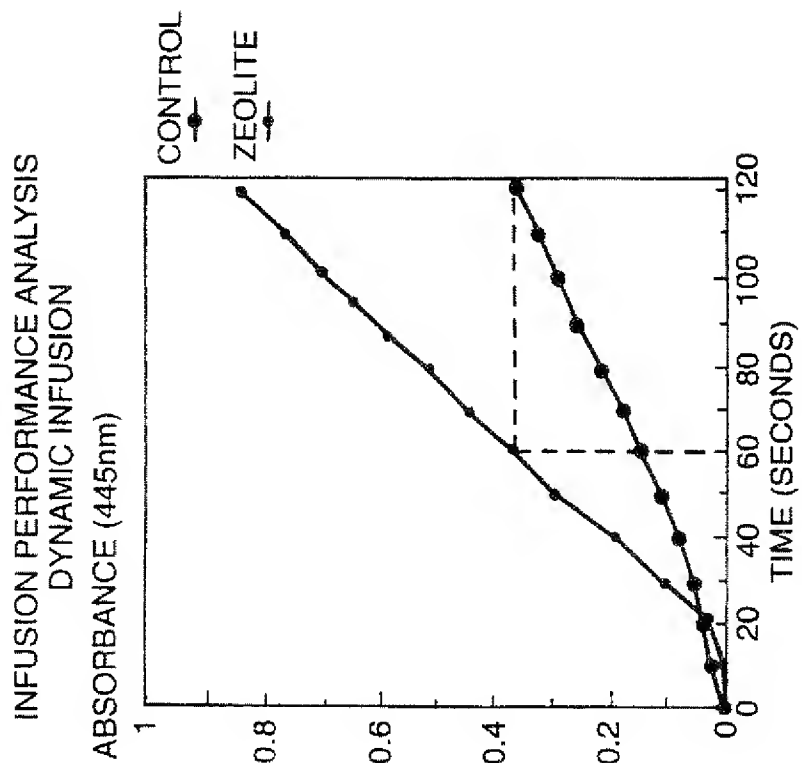
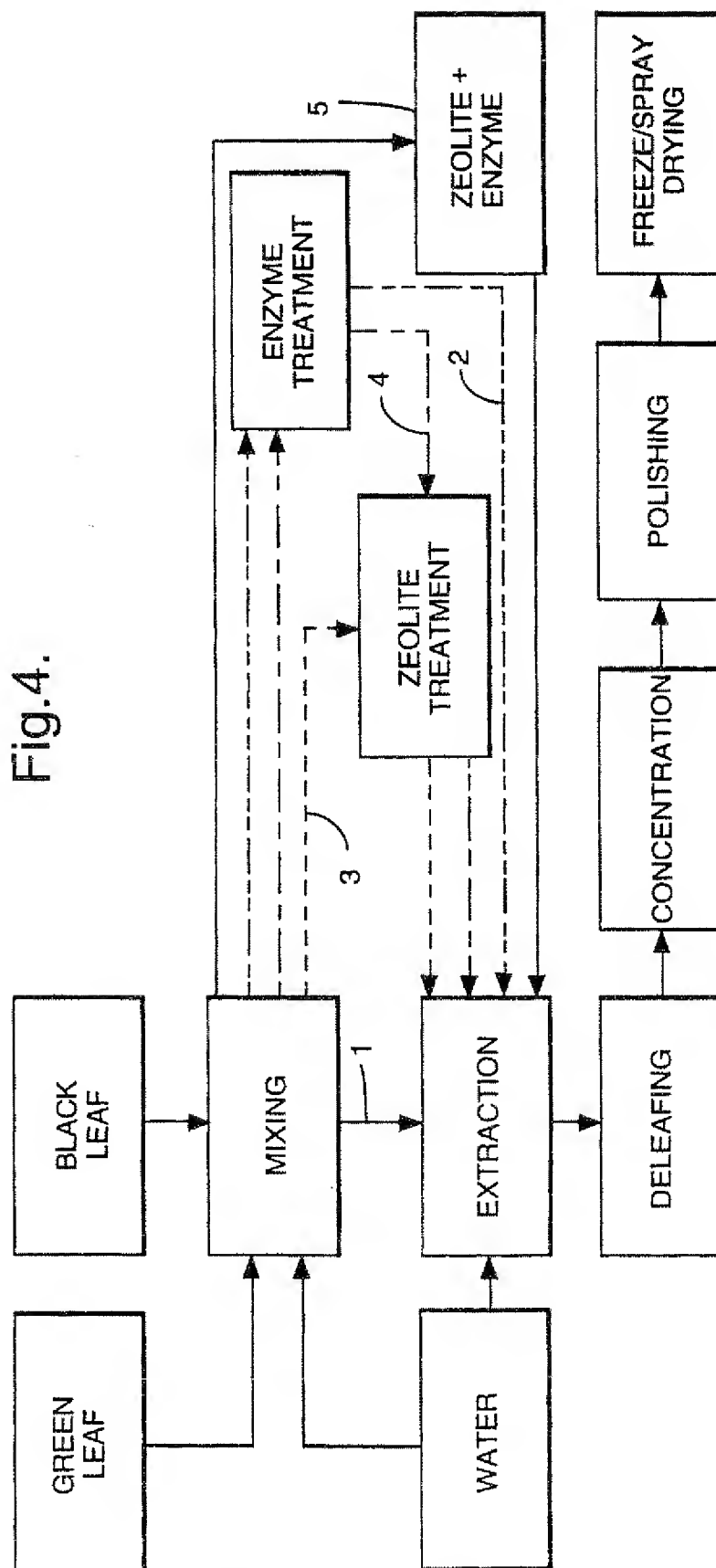


Fig.3B.





INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/01877

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A23F3/08 A23F3/14 A23F3/30 A23F3/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 9021 Derwent Publications Ltd., London, GB; AN 88-068844 XP002014421 & JP 63 024 850 A (SOFT SILICA KK) cited in the application see abstract	1,5-7, 12,15,16
A	DATABASE WPI Week 8622 Derwent Publications Ltd., London, GB; AN 86140037 XP002014423 & JP 61 074 527 A (OZAWA T) see abstract	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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PCT/EP 97/01877

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 108, no. 13, 28 March 1988 Columbus, Ohio, US; abstract no. 111228, T. MGALOBILISHVILI: "Effects of chelates and clinoptilolite-rich tuffs on biochemical indexes of tea leaf quality" XP002014420 see abstract & SOOBASHCH. AKAD. NAUK GRUZ. SSR, vol. 128, no. 2, 1987, pages 401-404, ---	1
A	DATABASE WPI Week 8819 Derwent Publications Ltd., London, GB; AN 88131290 XP002014424 & SU 1 342 470 A (GEOR SUBTROPICAL) cited in the application see abstract ---	1
A	FR 2 160 982 A (THE PROCTER & GAMBLE CO) 6 July 1973 see claims 1,37,38; example 14 ---	1
A	DATABASE WPI Week 9606 Derwent Publications Ltd., London, GB; AN 96054032 XP002014422 & JP 07 313 580 A (RELEASE KAGUKU KOGYO KK) see abstract ---	
A	US 4 051 264 A (G. SANDERSON) 27 September 1977 see claims 1-16; table 1 ---	13,14,19
P,A	EP 0 760 213 A (UNILEVER) 5 March 1997 see examples 5,6 ---	13,14,19
A	EP 0 013 451 A (UNION CARBIDE CO) 23 July 1980 cited in the application ---	
A	US 4 135 001 A (C. EDMONDS) 16 January 1979 ---	
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 234, 29 May 1992 & JP 04 049227 A (MASAICHI SAKURASHITA) see abstract -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 97/01877

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2160982 A	06-07-73	AT 329965 B	10-06-76
		AU 468195 B	08-01-76
		AU 4914272 A	23-05-74
		BE 791754 A	22-05-73
		CA 1004591 A	01-02-77
		CH 581585 A	15-11-76
		CH 554814 A	15-10-74
		DE 2256694 A	24-05-73
		DE 2265528 C	16-09-82
		GB 1382896 A	05-02-75
		JP 1141657 C	13-04-83
		JP 48061664 A	29-08-73
		JP 57033023 B	14-07-82
		NL 7215846 A,B,	24-05-73
		SE 427890 B	24-05-83
		SE 7612246 A	03-11-76
		US 3888998 A	10-06-75

US 4051264 A	27-09-77	AU 501876 B	05-07-79
		AU 1207976 A	22-09-77
		CA 1087446 A	14-10-80
		CH 622410 A	15-04-81
		DE 2610533 A	07-10-76
		GB 1546508 A	23-05-79
		IN 144499 A	13-05-78
		JP 51115999 A	13-10-76

EP 760213 A	05-03-97	NONE	

EP 13451 A	23-07-80	CA 1141229 A	15-02-83
		JP 55088806 A	04-07-80
		JP 60034404 B	08-08-85
		US 4331694 A	25-05-82

US 4135001 A	16-01-79	NONE	
